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ARL 63-126

**ELECTRON PARAMAGNETIC RESONANCE OF  
IMPURITIES OF SINGLE CRYSTALS AND  
OF SULFUR MONOXIDE**

*BARTH B. DORAIN*

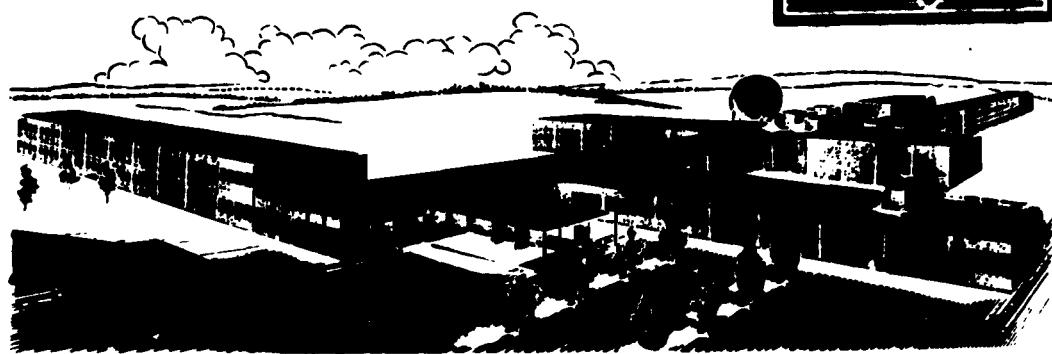
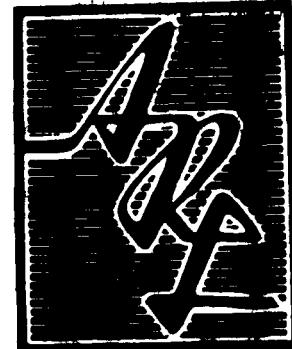
*BRANDEIS UNIVERSITY  
WALTHAM, MASSACHUSETTS*

JULY 1963

AEROSPACE RESEARCH LABORATORIES  
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SINGLE CRYSTALS AND OF SULFUR MONOXIDE**

*PAUL B. DORAIN*

*BRANDEIS UNIVERSITY  
WALTHAM, MASSACHUSETTS*

JULY 1963

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AEROSPACE RESEARCH LABORATORIES  
OFFICE OF AEROSPACE RESEARCH  
UNITED STATES AIR FORCE  
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

## FOREWORD

This final technical report was prepared by Brandeis University, Waltham, Mass., on contract AF33(616)6401 for the Aerospace Research Laboratories of the Office of Aerospace Research, United States Air Force. This work was accomplished on Project 7885, "Research in Solid State Physics" and Task 7385-03 "Semiconductor Research". The work reported herein covers the period 1 June 1961 to 31 May 1963.

Mr. Donald Locker of the Solid State Physics Laboratory, ARL, was the task scientist.

## ABSTRACT

This is the Final Technical Report on the theoretical and experimental properties of impurity ions in crystal lattices. The electron paramagnetic resonance experiments on  $\text{Re}^{+4}$  in  $\text{K}_2\text{PtCl}_6$ ,  $\text{Cd}^{+2}$  in  $\text{CdS}$ ,  $\text{Ag}^{+2}$  in  $\text{NaF}$  and  $\text{Cu}^{+2}$  in  $\text{LiF}$  are discussed. In addition the results for the electron paramagnetic resonance of  $\text{SO}$  are given along with a preparation of single crystals of  $\text{CdO}$ .

TABLE OF CONTENTS

SECTION	PAGE
I RHENIUM (+4) IN AN OCTAHEDRAL CUBIC ELECTRIC FIELD	1
A. THE CONFIGURATION OF $\text{Re}^{+4}$	1
B. THE CRYSTAL FIELD	1
C. GROUP THEORY	2
D. THE SPIN HAMILTONIAN	3
E. ROTATION MATRIX	4
F. CRYSTAL STRUCTURE	5
G. THE PARAMAGNETIC RESONANCE RESULTS	6
H. DISCUSSION OF PARAMETERS	7
II INVESTIGATION OF SULFUR MONOXIDE	14
III THE ELECTRON PARAMAGNETIC RESONANCE OF $\text{Cr}^{+2}$ IN A CdS SINGLE CRYSTAL	18
A. INTRODUCTION	18
B. THE ENERGY LEVEL OF $\text{Cr}^{+2}$	18
C. SPIN HAMILTONIAN	20
D. CRYSTAL STRUCTURE	20
E. RESULTS	23
F. DISCUSSION OF RESULTS	25
IV ANGULAR MODULATION OF MAGNETIC FIELDS IN PARAMAGNETIC RESONANCE EXPERIMENTS.	27
V CADMIUM OXIDE PREPARATION	30
A. INTRODUCTION	30
B. DESCRIPTION OF METHOD	30
C. ANALYSIS	30
D. OPTICAL MEASUREMENTS	31
E. RESONANCE RESULTS	31

VI	COPPER (II) AND SILVER (II) IN ALKALI FLUORIDES	32
A.	INTRODUCTION	32
B.	COPPER (II)	32
C.	SILVER (II)	32
D.	HYPERFINE INTERACTION	32
VII	REFERENCES	34
APPENDIX I. ARTICLES PUBLISHED UNDER CONTRACT		35

LIST OF ILLUSTRATIONS

FIGURE	PAGE
I.1 10Gc Resonance Results of $\text{Re}^{+4}$ in $\text{K}_2\text{PtCl}_6$	8
I.2 24Gc Resonance Results of $\text{Re}^{+4}$ in $\text{K}_2\text{PtCl}_6$	9
I.3 Energy Level Diagram for $\text{H} \parallel (111)$	11
III.1 Energy Level Diagram for D-state in Interstitial Site of CdS	19
III.2 Energy Level Diagram for Various D/a Ratios	21
III.3 Magnetic Field Splittings for $\text{D}/\text{a} = 0.9$ , $\cos \theta = 1$	22
III.4 Experimental Results for $\text{Cr}^{+2}$ in CdS at $\lambda = 1 \text{ cm.}$	24
IV.1 Angular Modulation Fields	27
IV.2 Angular Modulation Measurements	29

## I. RHENIUM (+4) IN AN OCTAHEDRAL CUBIC ELECTRIC FIELD.

Since 1959 when B. Bleaney published a paper<sup>(1)</sup> on the paramagnetic resonance of quartet states and their use as masers, there has been considerable interest in materials which might have the proper ground state. The attempts to find quartets have been almost completely unsuccessful because of the requirement that they can occur only in cubic electric fields. Jahn-Teller distortions generally prevent pure cubic fields from existing about an ion with more than two fold degeneracy in its ground state.

It appeared that  $\text{Re}^{+4}$  in a single crystal of  $\text{K}_2\text{PtCl}_6$  might possibly have a quartet state lowest and for this reason, crystals were grown with concentrations of  $\text{Re}^{+4}$  ranging from 0.1 to 5%. Electron paramagnetic resonance measurements were carried out and a theoretical analysis was performed.

The work described is essentially that of the Ph.D. Thesis of Mr. Ronald Rahn which will be submitted during the Spring of 1963 to the Faculty of Brandeis University. The work has been briefly described in a note to the Journal of Chemical Physics, and a more complete description will be given later in a journal.

### A. THE CONFIGURATION OF $\text{Re}^{+4}$ .

Rhenium has an electronic configuration of  $5d^3$  in the +4 oxidation state. It is therefore expected that the radical wave function will have a large spacial extent and that the spin orbit interaction will be large.

### B. THE CRYSTAL FIELD.

In a cubic octahedral environment, d wavefunctions have some degeneracy removed. A three-fold degenerate state consisting of the functions which transform like  $xy$ ,  $yz$ , and  $zx$  is lower and a doublet consisting of the functions

$3z^2 - r^2$  and  $x^2 - y^2$  is higher. Pictorially this is seen to arise because the triplet functions correspond to d electrons being in orbits which minimize the electrostatic repulsion between the electrons and the ligands. The situation is diagrammed in Figure I.1

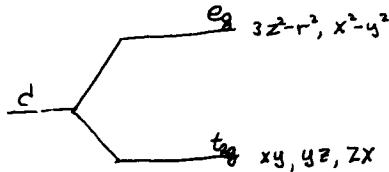


Figure I.1

The doublet is frequently called the  $e_g$  orbital and the triplet the  $t_{2g}$  orbital.

The three 5d electrons of  $\text{Re}^{+4}$  will distribute themselves in the  $t_{2g}$  orbital because the energy difference between  $t_{2g}$  and  $e_g$  is  $\sim 10^4 \text{ cm}^{-1}$ . It may be shown<sup>(2)</sup> that if just the  $t_{2g}$  orbitals, namely  $xy$ ,  $yz$  and  $zx$  are considered, there is an isomorphism between terms arising from a  $p^n$  configuration and a  $t_{2g}^{6-n}$  configuration. The isomorphism is complete if the angular momentum operator,  $L$ , in the  $p^n$  configuration is replaced by  $-L$ . That is, if  $L_z$  operates on a  $t_{2g}^{6-n}$  configuration, it has the same matrix as  $-L_z$  operating on a  $p^n$  configuration.

The advantage of working with a  $p^n$  configuration is that it is easy to calculate the terms which arise. For instance, for  $\text{Re}^{+4}$ , we consider a  $t_{2g}^3$  configuration which is isomorphous with a  $p^3$  configuration. A  $p^3$  configuration gives rise to a  $^4S$ , a  $^2D$  and a  $^2P$  state with the quartet S state lowest by Hund's rules. It is this quartet with which we will be concerned.

### C. GROUP THEORY.

An analysis of group theory tables shows that only in the cubic group can a four fold degenerate representation arise. For groups with lower symmetry, the highest degeneracy is two-fold. It is easy to see that "good" cubic environments are necessary to observe quartets.

The four-fold degenerate representation is called in the Bethe notation,  $\Gamma_8$ . Since we are interested in a Hamiltonian which is invariant under the operations of the cubic group and transforms like  $\Gamma_1$  (i.e.,  $\underline{S} \cdot \underline{H}$  in a Zeeman term which transforms like a scalar). We must examine the direct product:

$$\Gamma_8 \times \Gamma_8$$

to obtain the number of times  $\Gamma_1$  is contained therein. It is found that  $\Gamma_1$  is contained twice, and therefore by Schur's Lemma, there must be at most two terms in the Hamiltonian.

#### D. THE SPIN-HAMILTONIAN.

From the group theory it is seen that a two term Hamiltonian which transforms like  $\Gamma_1$  will adequately describe the Zeeman splitting of a  $\Gamma_8$  state. Certainly a term of the form  $H' = g\beta \underline{H} \cdot \underline{S}$  has the proper symmetry. It is only necessary to find other polynomials in  $\underline{S}$  which have the same transformation properties as  $\underline{S}$  in  $\Gamma_1$  to obtain the second term. Since  $\underline{S}$  transforms like  $\Gamma_4$ , the polynomials must also transform like  $\Gamma_4$ . The operator equivalents to these polynomials are given by Griffith<sup>(2)</sup> and are:

$$\begin{aligned} S_x^3 - 1/15 (\underline{S} \cdot \underline{H}) (3\underline{S}^2 - 1) & \quad \text{which transforms like } S_x \\ S_y^3 - 1/15 (\underline{S} \cdot \underline{H}) (3\underline{S}^2 - 1) & \quad " \quad " \quad " \quad S_y \\ S_z^3 - 1/15 (\underline{S} \cdot \underline{H}) (3\underline{S}^2 - 1) & \quad " \quad " \quad " \quad S_z \end{aligned}$$

The Hamiltonian is therefore,

$$H_e = g\beta \underline{H} \cdot \underline{S} + \mu\beta \{ H_x S_x^3 + H_y S_y^3 + H_z S_z^3 - 1/5 (\underline{S} \cdot \underline{H}) (3\underline{S}^2 - 1) \} \quad (I.1)$$

The parameters  $g$  and  $\mu$  are determined by experiment. The first term has full spherical symmetry while the second term reduces the symmetry to cubic. It may be anticipated that the energy is therefore anisotropic because of the term in  $\mu$ .

$\text{Re}^{185}$  and  $\text{Re}^{187}$  both have nuclei with approximately equal magnetic moments and nuclear spins of  $5/2$ . Therefore the Hamiltonian of Equation I.1 is compli-

cated by the interaction of the electron spin with the nuclear spin. Since the nuclear spin,  $I$ , has the same transformation properties as  $H$  or  $S$ , that is it transforms like  $\vec{r}_i$ , the nuclear spin-electron spin Hamiltonian may be quickly written as,

$$H_n = A \underline{I} \cdot \underline{S} + \bar{v} [I_x^3 S_x^3 + I_y^3 S_y^3 + I_z^3 S_z^3 - 1/5 (\underline{I} \cdot \underline{S})(3S^2 - 1)] \quad (I.2)$$

which must be added to Equation I.1. Terms higher than 1st power of  $I$  have been ignored because the coefficients will be extremely small.

In general, the total Hamiltonian will not be diagonal in  $H$  except for the case where  $H = k H_z$ . Since the term in  $g$  is expected to be the largest, it is of help to rotate the Hamiltonian consisting of  $H_e + H_n = H_t$  so that in the new coordinate system  $\underline{H} \cdot \underline{S}$  is always diagonal.

#### E. ROTATION MATRIX.

To rotate an irreducible tensor,  $T_n^m$  it is only necessary to calculate the rotation matrices of the full rotation group  $D_{m'm}^n (\alpha \beta \gamma)$  where  $\alpha$ ,  $\beta$  and  $\gamma$  are the Euler angles describing the rotation of the coordinate system. The rotated Hamiltonian is then

$$H_t' = R T_n^m R^{-1} = \sum_{m'} D_{m'm}^n (\alpha \beta \gamma) T_{m'}^n \quad (I.3)$$

It remains to express  $H_t' = H_e + H_n$  in terms of irreducible tensors,  $T_{m'}^n$ . This is most easily done by the use of tables given by Griffith<sup>(2)</sup> in his Appendix 19.

The Hamiltonian becomes:

$$\begin{aligned} H = g \beta [H_z S_z + \frac{1}{\sqrt{2}} (H_+ T_{-1}^1 - H_- T_1^1)] \\ + \mu \beta [H_z T_0^3 (S) - \frac{1}{\sqrt{2}} H_+ (\sqrt{5/8} T_3^3 (S) + \sqrt{3/8} T_{-1}^3) \\ + \frac{1}{\sqrt{2}} H_- (\sqrt{5/8} T_{-3}^3 (S) + \sqrt{3/8} T_1^3)] \end{aligned}$$

\* identical terms found by replacing  $H_i$  with  $I_i$  and substitution of the equivalent

irreducible tensor expression.

(I.4)

where  $T_1^1(S) = -\frac{1}{12}S_+$ ,  $T_0^1(S) = S_z$ ,  $T_{-1}^1(S) = \frac{1}{12}S_-$   
 $T_3^3(S) = -\frac{1}{18}S_+^3$ ,  $T_{-3}^3(S) = \frac{1}{18}S_-^3$   
 $T_2^3(S) = -\frac{\sqrt{3}}{14}S_+^2(1+S_z)$ ,  $T_{-2}^3(S) = \sqrt{3/4}S_-^2(1+S_z)$   
 $T_1^3(S) = -\frac{1}{\sqrt{30}}S_+ \left[ 3 - 3/2S_-^2 + \frac{15}{2}S_z + \frac{15}{2}S_z^2 \right]$   
 $T_{-1}^3(S) = \frac{1}{\sqrt{30}}S_- \left[ 3 - 3/2S_-^2 - \frac{15}{2}S_z + 15/2S_z^2 \right]$   
 $T_0^3(S) = \frac{1}{\sqrt{10}} \left[ 5S_z^3 - 3S_-^2S_z + S_z \right]$

and tensors in I and H have the same form.

The rotation matrix elements are given in Table I.1. Upon transformation through the angles  $\alpha = \pi/4$ ,  $\beta = \beta$ ,  $\gamma = -\pi/4$ , the Hamiltonian has the form:

$$H = g H_z + A(I_z S_z + 1/2(I_- S_+ + I_+ S_-)) \quad (I.5)$$

$$\begin{aligned}
 & + 5 \left[ F_1(\mu\beta H_z + UI_z) + F_2 UI_+ - F_3 UI_- \right] S_+^3 \\
 & + 5 \left[ F_1(\mu\beta H_z + UI_z) + F_2 UI_- + F_3 UI_+ \right] S_-^3 \\
 & + 30 \left[ F_4(\mu\beta H_z + UI_z) + F_5 UI_+ - F_6 UI_- \right] S_+^2(1+S_z) \\
 & + 30 \left[ F_4(\mu\beta H_z + UI_z) + F_5 UI_- + F_6 UI_+ \right] S_-^2(1-S_z) \\
 & + 2 \left[ F_7(\mu\beta H_z + UI_z) + F_8 UI_+ - F_9 UI_- \right] S_+ \left( 3 - 3/2S_-^2 + 15/2S_z + 15/2S_z^2 \right) \\
 & + 2 \left[ F_7(\mu\beta H_z + UI_z) - F_8 UI_- + F_9 UI_+ \right] S_- \left( 3 - 3/2S_-^2 - 15/2S_z + 15/2S_z^2 \right) \\
 & + 4 \left[ F_{10}(\mu\beta H_z + UI_z) + F_{11} U(I_+ + I_-) \right] \left[ 5S_z^3 - 3S_-^2S_z + S_z \right]
 \end{aligned}$$

where

$$\begin{aligned}
 F_1 &= 2 \cos \beta \sin \beta (3 \sin^2 \beta + 2) & F_7 &= 10 \cos \beta \sin \beta (3 \cos^2 \beta - 1) \\
 F_2 &= (3 \cos^2 \beta - 1)(\cos^2 \beta - 3) & F_8 &= 5F_3 \\
 F_3 &= \sin^2 \beta (3 \cos^2 \beta - 1) & F_9 &= -1 - 10 \cos^2 \beta + 15 \cos^4 \beta \\
 F_4 &= 2F_3 & F_{10} &= 8(1 - 15 \sin^2 \beta + 15/4 \sin^4 \beta) \\
 F_5 &= 1/2 F_1 & F_{11} &= 5F_6 \\
 F_6 &= \sin \beta \cos \beta (3 \cos^2 \beta - 1)
 \end{aligned}$$

The eigen values for  $S = 3/2$  and  $I = 5/2$  are to 1st order:

$$E_{Mm} = g \beta HM + 4 F_{10} \mu \beta H (5M^3 - 4I/4 M) + AMm + 4 F_{10} Um (5M^3 - 4I/4 M) \quad (I.6)$$

Complete second and higher order perturbation calculations are only practical for specific values of  $\beta$ , namely when  $H$  is parallel to the following axes of the crystal: (111), (100) and (110). For  $H$  (111) the second order correction is:

$$\left[ \frac{A}{2} + \frac{U}{20} (- 7/4 - 5M + 5M^2) \right]^2 - \frac{(3/2 + M)(5/2 - M)(5/2 - m)(7/2 + m)}{g H + A(M - m - 1)} \\ - \left[ \frac{A}{2} + \frac{U}{20} (- 7/4 + 5M + 5M^2) \right]^2 - \frac{(3/2 - M)(5/2 + M)(5/2 + m)(7/2 - m)}{g H + A(-M + m - 1)} \quad (I.7)$$

Higher order perturbations become more complex and are not given in this report.

#### F. CRYSTAL STRUCTURE.

Single crystals of  $K_2PtCl_6$  were grown containing 0.1, 0.3, 1.0 and 5.0% of  $Re^{+4}$ .  $K_2PtCl_6$  is a face-centered cubic lattice with  $a_0 = 9.755 \text{ \AA}$ . The isomorphous  $K_2PtCl_6$  has a cell constant of  $9.842 \text{ \AA}$ . Each transition metal ion is surrounded by six chloride ions arranged at the corners of an octahedron with the metal ion in the center. Each  $PtCl_6^{4-}$  is surrounded by eight potassium ions arranged at the corners of a cube. Thus to a good approximation, a  $Re^{+4}$  ion "sees" a cubic electric field.

#### G. THE PARAMAGNETIC RESONANCE RESULTS.

Paramagnetic resonance experiments were made on single crystals of  $K_2PtCl_6$  containing 0.5%  $Re^{+4}$ . No resonance was observed except at temperatures of the boiling point of liquid helium and below. Measurements were made at microwave frequencies of 10Gc., 24Gc. and 35Gc. Detection was accomplished with a 100 Kc modulation system.

The angular variation,  $\beta$ , for the electron resonance as a function of

magnetic field is shown in Figures I.1 and I.2 for 10Gc. and 24Gc. Lines corresponding to  $\Delta M = \pm 1$  and  $\Delta m = 0$  transitions are clearly visible at either frequency. The lines corresponding to  $\Delta M = \pm 1$  and  $\Delta m = \pm 1$  and  $\Delta m = \pm 2$  are broad and at some angles not distinguishable.

The experimental results for  $\Delta M = \pm 1$ ,  $\Delta m = 0$  transitions are found using the eigenvalues of Equations I.6 and I.7 to be:

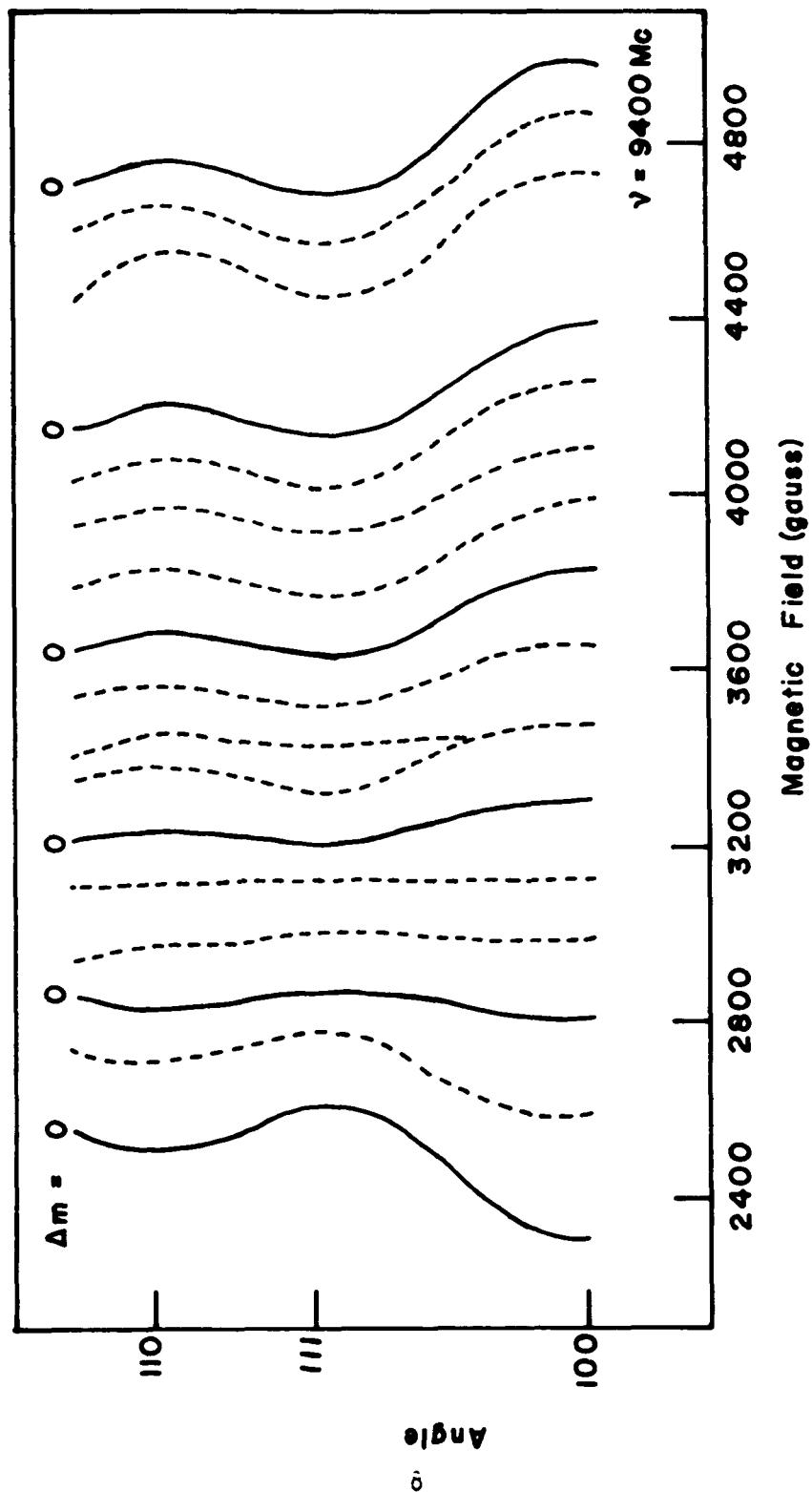
Wavelength	g	u	A( $\text{cm}^{-1}$ )	$U(\text{cm}^{-1})$
3 cm	1.8124	$-8.1 \times 10^{-3}$	$3.94 \times 10^{-2}$	$-3.2 \times 10^{-3}$
1 cm	1.8151	$-13.0 \times 10^{-3}$	$3.93 \times 10^{-2}$	$-3.8 \times 10^{-3}$
8 mm	1.8140	$-13.0 \times 10^{-3}$	$3.97 \times 10^{-2}$	$-3.9 \times 10^{-3}$
average	1.8138	$-11.4 \times 10^{-3}$	$3.95 \times 10^{-2}$	$-3.6 \times 10^{-3}$

From the  $\Delta M = \pm 1$ ,  $\Delta m = \pm 1$  transitions a value for the nuclear quadrupole coupling should be obtainable. However because of the broadness of the lines, the uncertainty in the peak positions is approximately the size of the effect. If the quadrupole term is written as  $P(I_z^2 - 1/3 I(I+1))$  the value of P seems to be approximately  $2 \times 10^{-4} \text{ cm}^{-1}$ .

Using the determined parameters, an energy level diagram was constructed for the case where H is parallel to the (111) axis for values of H from 0 to 15,000 gauss. This diagram is shown in Figure I.3, which clearly indicates that transitions of less than 10,000 Mc/s will occur in a complicated region of the spectrum. Broad transitions were observed at field of about 700 to 2000 gauss at a frequency of 10,000 Mc/s. These lines are due to  $\pm 3/2$  to  $\pm 1/2$  transitions. At the present time, they cannot be unambiguously identified for particular transitions.

#### H. DISCUSSION OF PARAMETERS.

In 1961 J. C. Eisenstein published a study of the magnetic and optical absorption spectrum of  $\text{K}_2\text{PtCl}_6^{(3)}$ . His approach was to explain the optical spectrum and magnetic susceptibility by a description of the  $\text{Re}^{+4}$  ion in terms of a set of



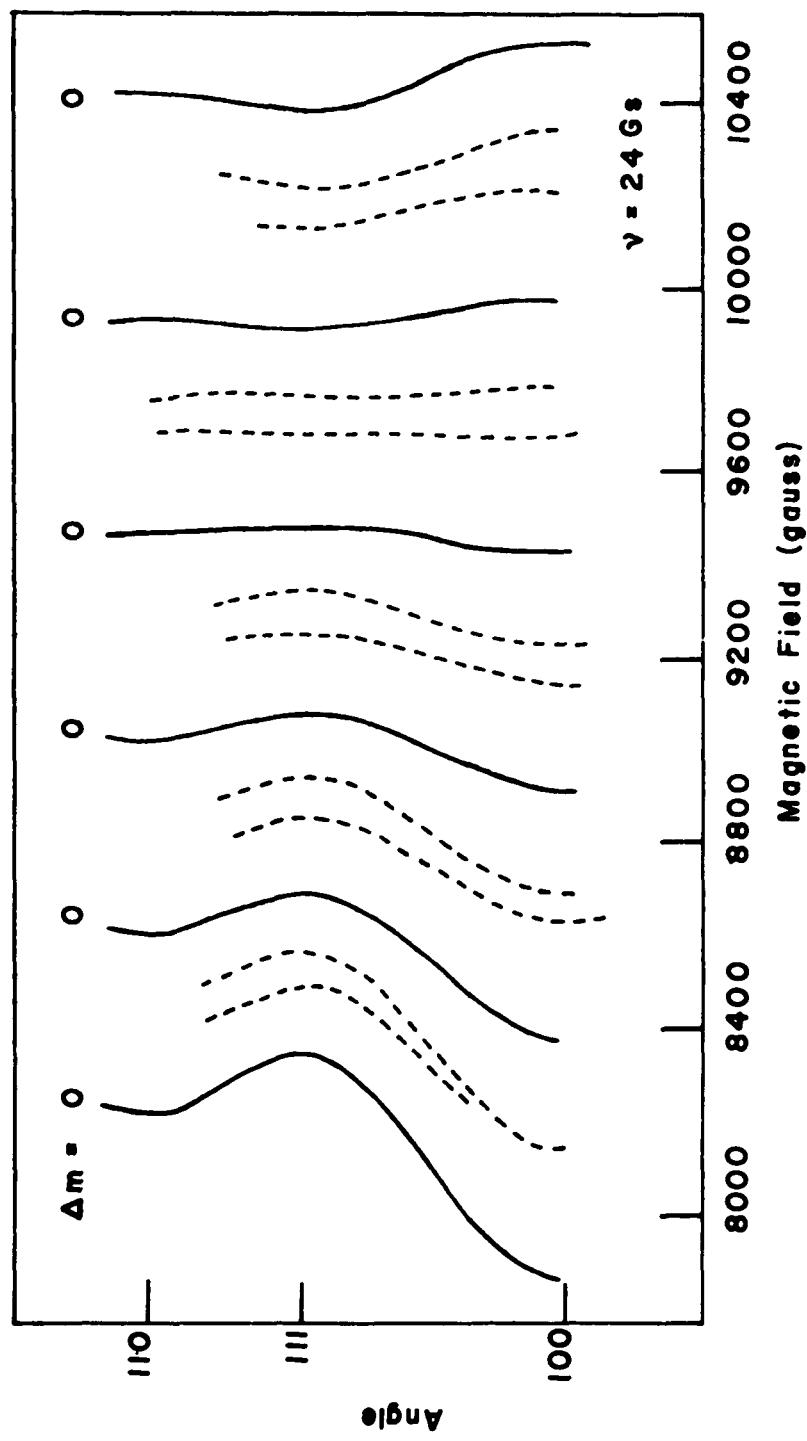


Figure 1.2

parameters which includes the strength of the octahedral ligand field, the Coulomb integrals, the spin-orbit coupling constant and orbital reduction factors. He gave the complete  $9 \times 9$ ,  $9 \times 9$  and  $21 \times 21$  matrices which he diagonalized by means of machine computer techniques to obtain agreement with the optical spectrum.

If Eisenstein used his values of the crystal field energy ( $\sim 33,500 \text{ cm}^{-1}$ ) and the spin orbit coupling constant ( $\sim 2300 \text{ cm}^{-1}$ ), an expression for the magnetic moment matrix elements for the levels belonging to the ground state  $\Gamma_8$  level was calculated using instead of  $\beta(\underline{L} + 2\underline{S}) \cdot \underline{H}$ , a reduced orbital angular momentum magnetic moment operator  $\beta(\underline{kL} + 2\underline{S}) \cdot \underline{H}$ . His results are:

$$\begin{aligned} \langle D | \mu_z | D \rangle &= 0.96858 - 0.12374(K_\gamma K_\epsilon)^{1/2} - 0.01288K_\epsilon \\ \langle C | \mu_z | C \rangle &= 2.90017 - 0.25507(K_\gamma K_\epsilon)^{1/2} - 0.03268K_\epsilon \end{aligned} \quad (I.8)$$

where D belongs to  $M = \pm 3/2$  and C to  $\pm 1/2$ . If we use the spin-Hamiltonian of Equation I.1 we can calculate g and u in terms of the orbital reduction factors. The expressions are:

$$\begin{aligned} g &= 1.93382 - 0.17779(K_\gamma K_\epsilon)^{1/2} - 0.02138K_\epsilon \\ u &= 0.001856 + 0.03875(K_\gamma K_\epsilon)^{1/2} - 0.001599K_\epsilon \end{aligned} \quad (I.9)$$

If we substitute  $K_\gamma = K_\epsilon = 0.600$ , the values of g and u are 1.8143 and +0.0202 respectively.

The agreement of the g value calculation with the measured g value supports the interpretation of Eisenstein. Unfortunately, the sign of the u parameter is opposite the measured value.

McGarvey<sup>(4)</sup> and Eisenstein have suggested that a small axial component of the electric field may exist. McGarvey has calculated this contribution to resonance field of the  $-1/2$  to  $+1/2$  transitions and finds that it has the same angular dependence as u but opposite sign. The contribution to u is:

$$-1/2 (D/g\beta H)^2$$

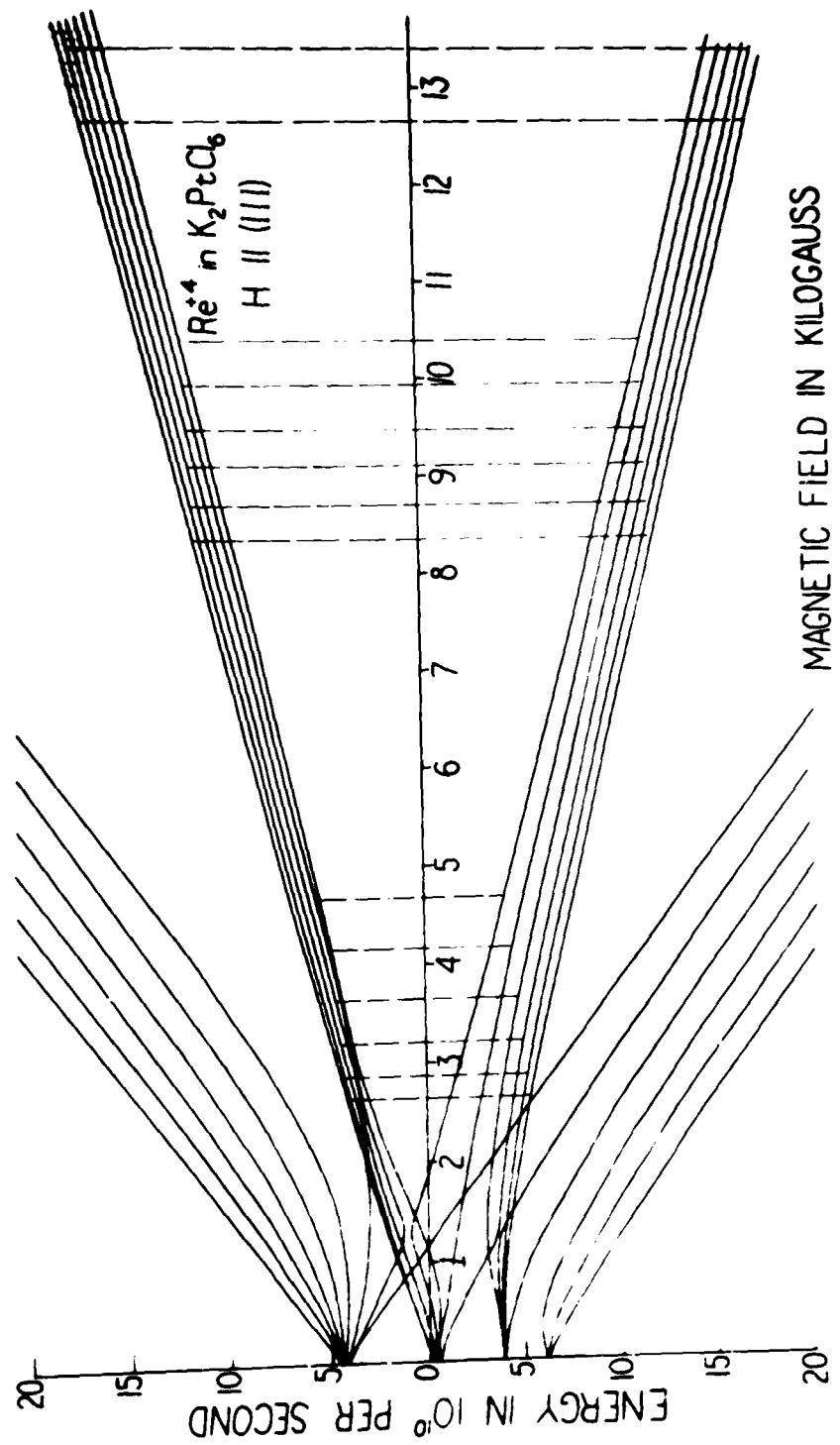


Figure 1.3

and should be frequency dependent. The measured values of  $u$  are found to be essentially constant and even the variation is opposite to that expected on the bases of McGarvey's calculation. However if the value of  $u$  arises from a  $D$  term,  $D$  will be about  $0.05 \text{ cm}^{-1}$ . More work needs to be done on the interpretation of the measured data.

Table I.1

$(m')$	3	2	1
3	$\frac{1}{8}(\cos \beta + 1)^3$	$-\frac{(6)^{1/2}}{8} \sin \beta (\cos \beta + 1)^2$	$(15)^{1/2}(\cos \beta + 1)(\sin \beta)^2$
2	$-\frac{(6)^{1/2}}{8} \sin \beta (\cos \beta + 1)^2$	$\frac{1}{4}(\cos \beta + 1)^2(3\cos \beta - 2)$	$-(10)^{1/2} \sin \beta \cdot$ $(3\cos \beta - 1)(\cos \beta + 1)$
1	$-\frac{(15)^{1/2}}{8}(\cos \beta + 1)(\sin \beta)^2$	$\frac{(10)^{1/2}}{8} \sin \beta (1 + \cos \beta) \cdot$ $(3\cos \beta - 1)$	$\frac{1}{8}(\cos \beta + 1)^3$ $-\frac{1}{4}(\sin \beta)^2(7\cos \beta + 1)$
0	$-\frac{(5)^{1/2}}{4}(\sin \beta)^3$	$-\frac{(30)^{1/2}}{4}(\sin \beta)^2 \cos \beta$	$-\frac{(3)^{1/2}}{4} \sin \beta (5\sin^2 \beta - 4)$

$$d_{m'm}^j(\beta) = (-1)^{m'-m} d_{mm'}^j(\beta)$$

$$d_{m'm}^j(\beta) = d_{-m,-m'}^j(\beta)$$

$$d_{m'm}^j(\beta) = (-1)^{m'-m} d_{-m-m'}^j(\beta)$$

## II. INVESTIGATION OF SULFUR MONOXIDE.

The electron paramagnetic resonance of SO radical is currently under investigation.

Whereas the emission band spectrum<sup>(7)</sup> of this molecule has been known for many years, only recently has the absorption spectrum been measured by flash photolysis<sup>(8)</sup>. It is found that upon flashing SO<sub>2</sub> the absorption spectrum of the parent molecule temporarily disappears and that the absorption spectrum of SO appears with a duration of several milliseconds.

By using a high conductance liquid nitrogen trap backed up by a large mechanical pump, a gas at low pressure can be pumped several cm in a millisecond. The present work is an attempt to prepare SO by a microwave discharge of SO<sub>2</sub> and to pump the SO into a detection cavity to measure the electron paramagnetic resonance. For this purpose a TE<sub>011</sub> rectangular discharge cavity resonating at 2450 Mc/sec powered by a diathermy magnetron is connected to a TE<sub>011</sub> cylindrical X-band detection cavity by a 1 cm quartz tube. At a pressure of 4 mm Hg with the discharge cavity a few cm removed from the detection cavity, the afterglow extends beyond the detection cavity.

Signals attributed to SO have been observed. The lines are of order 20 gauss wide and of intensity about equal to that of the weakest lines observed in O<sub>2</sub> by Tinkham and Strandberg<sup>(9)</sup>. The magnetic field positions of these lines are given as follows:

(kmc/sec)	H <sub>1</sub> (gauss)	H <sub>2</sub>	H <sub>3</sub>
8.899	2763	4498	5795
9.064	2654	--	5616
9.546	2292	3719	--
9.837	2165	3511	--

The shift of the lines to lower field with increase in frequency indicated that the levels involved in the transitions are converging with increasing field.

As outlined by Van Vleck<sup>(10)</sup> the effective Hamiltonian for a molecule in a  $^3\Sigma$  electronic state in a given state  $v$  is:

$$H = B_v [J(J + 1) + S(S + 1) - 2J \cdot S] + 2/3 \lambda (3S_z^2 - S^2) + \gamma K \cdot S + g \beta S \cdot H \quad (II.1)$$

The first three terms are due to rotation. The fourth term includes spin-spin and spin-orbit interactions. The fifth term is the spin-rotation interaction. The last term involves the interaction of the spin with an external magnetic field. It is the fourth and fifth terms which give rise to the splitting of the triplet.

Matrix elements of the Hamiltonian II.1 are most easily obtained using Hund's case a wave functions. In the absence of an external field the Hamiltonian is diagonal in  $J$  and  $S$ , but not in  $\Sigma$ . The last term is off diagonal in  $J$  and  $\Sigma$ . Diagonalization of the  $3 \times 3$  matrix for given  $J$ ,  $S = 1$ ,  $\Sigma = 1, 0, -1$  yields in the absence of the field Hund's case b energies. Henry<sup>(11)</sup> has brought in the off diagonal elements for  $O_2$  by a second diagonalization of the resulting case b  $3 \times 3$  matrix for  $K = J + 1, J, J - 1$ .

Tinkham and Strandberg<sup>(9)</sup> use the more elaborate Van Vleck transformation. The question of which method to use in handling the off diagonal elements hinges upon the magnitude of  $\lambda$ . For large splitting second order perturbation theory is quite adequate.

Whereas Martin performed a rotational analysis for SO, he was unable to obtain  $\lambda$  for the ground state. It is normally quite difficult to extract reliable values of the splitting constants from  $^3\Sigma - ^3\Sigma$  spectra. Recently Barrow<sup>(12)</sup> has obtained  $\lambda = 11.69 \text{ cm}^{-1}$  for  $S_2$  and  $\lambda = 43 \text{ cm}^{-1}$  for  $SeO$ . For  $O_2$ ,  $\lambda = 1.984 \text{ cm}^{-1}$ . Thus, for SO  $\lambda = 5-7 \text{ cm}^{-1}$  is a reasonable estimate.

At present Martin's data is being reexamined. Wave numbers of the lines of the (1,6), (0,6), (0,7), (0,8), (0,9), (0,10) and (0,11) bands are given in

his Table I. The value of  $v''$  is increased by 2 over the original numbering as necessitated by Norrish and Oldershaw's <sup>(8)</sup> discovery of two lower bands.

In  $\Sigma - \Sigma$  systems the selection rules are  $K = \pm 1$ ,  $K' - K'' = +1$ ,  $-1$  transitions constitute the R and P branches respectively. Each level characterized by K is split into three levels,  $J + K + 1$ ,  $K$ ,  $K - 1$ , since  $J = \underline{K} + \underline{S}$ . The strongest lines occur where  $\Delta K = \Delta J$ . For given  $K''$  lines in both branches are given a subscript designation 1, 2, 3 corresponding to  $J'' = K'' + 1$ ,  $K''$ ,  $K'' - 1$  respectively.

The gross features of Martin's analysis are certainly correct. His assignment of  $K''$  is unquestioned. He made the assignments  $R_1$ ,  $R_3$ ,  $R_2$  and similarly in the P branch, for lines of given  $K''$  with decreasing wave number. The combination differences  $\Delta_2 F_1(K'') = R_1(K'' - 1) - P_1(K'' + 1)$ ,  $i = 1, 2, 3$  yield  $\Delta_2 F_3(K'') = \Delta_2 F_1(K'') \approx \Delta_2 F_2(K'')$ . This is indeed the situation in  $O_2$ . However, from calculations on SO using  $\lambda = 5.5$  and  $7 \text{ cm}^{-1}$  it has been observed that  $\Delta_2 F_1(K'') > \Delta_2 F_2(K'') > \Delta_2 F_3(K'')$ . The larger  $\lambda$  the greater is the difference. This behavior occurs in  $S_2$ .

If one makes the assignment in SO  $R_1$ ,  $R_2$ ,  $R_3$  and  $P_3$ ,  $P_2$ ,  $P_1$  the combination differences lie in the right order. Further,  $\Delta_2 F_2(K'')$  is found to be independent of  $\lambda$  as predicted by the theory.

To date only the (0,6) band has been fully analyzed. It is planned to promptly complete work on the other bands. The values of  $\lambda$  and  $\gamma$  will then be fitted by computer calculation to  $\Delta_2 F_1$  and  $\Delta_2 F_3$ . The rotational constants and splitting constants in both the upper and lower states can be obtained by this method. Publication of a note concerning these results is anticipated.

The calculation of the energies and wave functions from the diagonalization of the Hamiltonian over case a wave functions has been carried out on the RPC 4000 computer for  $\lambda = 5.5$  and  $7 \text{ cm}^{-1}$ ,  $J = 0$  to 8. It appears that for most transitions fields in excess of 10 Kgauss will be necessary to observe resonances

with X-band frequencies. These transitions at S-band lie at fields accessible to the magnet with a 2.5 inch gap. An S-band cavity system is currently being designed.

Identification of the already observed X-band lines is dependent upon obtaining  $\lambda$  from Martin's data. These lines appear not to be  $\Delta K = 0$ ,  $\Delta J = 0$  transitions as evidenced by the convergence with increased field.

### III. THE ELECTRON PARAMAGNETIC RESONANCE OF $\text{Cr}^{+2}$ IN CdS SINGLE CRYSTALS.

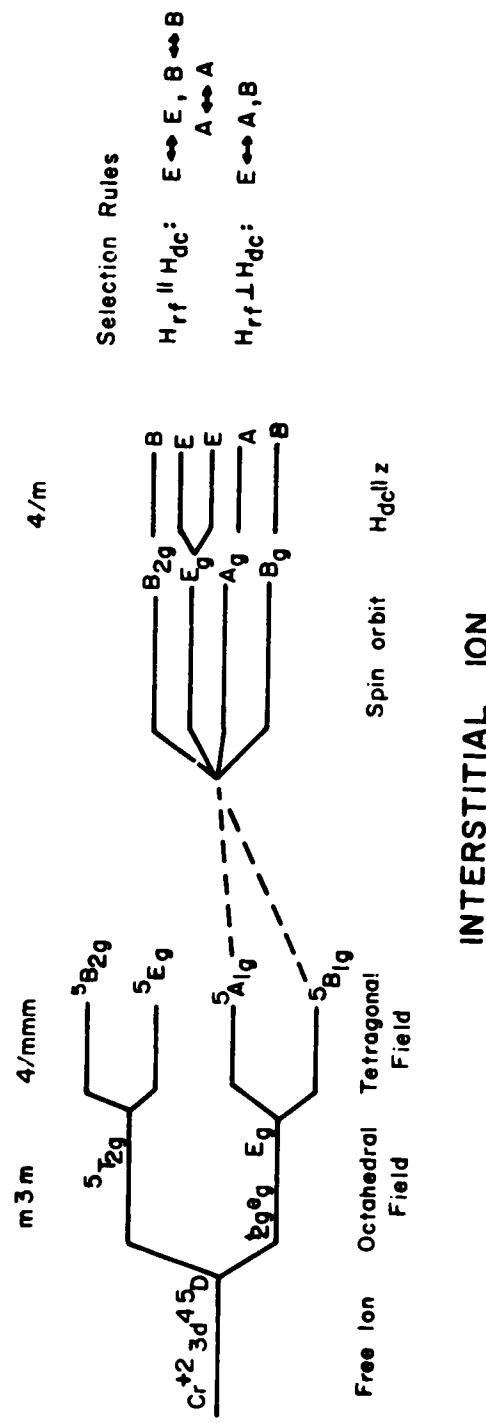
#### A. INTRODUCTION.

The electron paramagnetic resonance of  $\text{Cr}^{+2}$  in single crystals of cadmium sulfide has been measured at the boiling point of liquid helium. Simultaneously the same system was independently studied by T. Estle of Texas Instruments Company. The interpretations of the data are different and each has its difficulties. We report here the interpretation that the  $\text{Cr}^{+2}$  ions is an interstitial ion whereas the other interpretation is that the  $\text{Cr}^{+2}$  ion is substitutionally located with a small axial distortion.

#### B. THE ENERGY LEVEL OF $\text{Cr}^{+2}$ .

Chromium (+2) has the electron configuration of  $d^4$  which gives rise to a Hund ground state,  $^5D$ . Under the influence of an octahedral cubic field this state is split into an orbital triplet and a doublet with the doublet lowest. If the cubic field arises from a tetrahedral charge distribution, the triplet is lowest. Axial distortions along the cubic axes of the octahedral charge distribution remove the remaining degeneracy and an orbital singlet lies lowest. The ground state has five-fold spin degeneracy which is removed by spin-orbit interaction with higher states. Paramagnetic resonance if it is to be observed will occur among these states. However since there is an even number of electrons, the lowest spin state may also be a singlet and no resonance absorption will occur. The energy level scheme is shown in Figure III.1.

If a tetrahedral field is used the orbital triplet is split into three orbital singlets when a rhombohedral field is superimposed. The spin pentuplet will also split into five singlets and paramagnetic resonance may be observed between these levels if the frequency used matches the splitting. Again because it is an even electron system, there are not necessarily any degenerate levels.



**Figure III.1**

### C. SPIN HAMILTONIAN.

The spin Hamiltonian used to describe the octahedral case ground orbital singlet is:

$$H = \underline{S} \cdot \underline{g} \cdot \underline{H} + D \left\{ S_z^2 - 1/3 S(S+1) \right\} + a/6 \left\{ S_x^4 + S_y^4 + S_z^4 - 1/5 \underline{S}^2 (3S^2 + 3S - 1) \right\} \quad (\text{III.1})$$

with  $S = 2$ . The  $5 \times 5$  matrix may be solved for  $D \gg g \beta H$  with the eigen values

$$\begin{aligned} E_1 &= -D - 2/5^2 + G \cos \theta \\ E_2 &= -2D - 3/5^2 \\ E_3 &= -D - 2/5^2 - G \cos \theta \\ E_4 &= 2D + a/10 + (a^2/4 + 4G^2 \cos^2 \theta)^{1/2} \\ E_5 &= 2D + a/10 - (a^2/4 + 4G^2 \cos^2 \theta)^{1/2} \end{aligned} \quad (\text{III.2})$$

where  $\theta$  is the angle between the magnetic field and the tetragonal symmetry axis. The eigen values are plotted in Figure III.2 for positive and negative ratios of  $D/a$  for zero magnetic field and in Figure III.3 for  $\cos \theta = 1$  as a function of magnetic field for  $D/a = 0.9$ .

### D. CRYSTAL STRUCTURE.

Cadmium sulfide crystallizes in the Wurtzite lattice. Each cadmium is surrounded by four sulfides arranged at the corner of a tetrahedron with the cadmium in the center. Thus if the  $\text{Cr}^{+2}$  were substitutional, the energy level diagram would correspond to the tetrahedral case discussed above. However, the wurtzite lattice is an "open" lattice with large interstitial positions with a radius of about  $1.4 \text{ \AA}$  assuming covalent radii. Thus there is plenty of room for an interstitial ion. In this case each site is surrounded by six sulfide ions arranged in the form of an octahedron. There are two inequivalent sites in each lattice. The axis of the octahedron is inclined to the C-axis of the crystal by  $54^\circ$ . Thus the resonance should show four-fold symmetry if the crystal is oriented such that one of the octahedral cubic axes is the rotational axis; the other octahedral site will

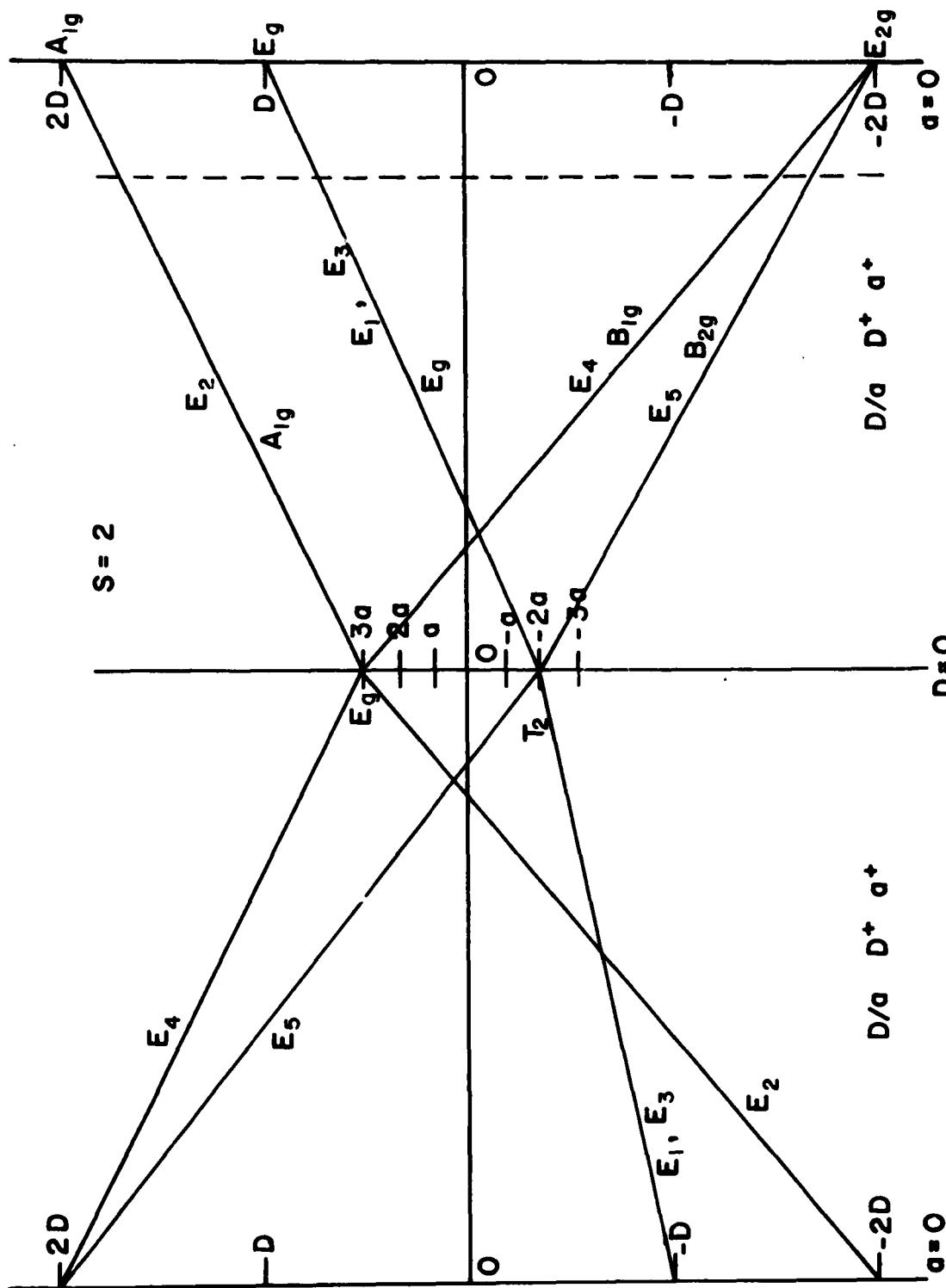


Figure m1.2

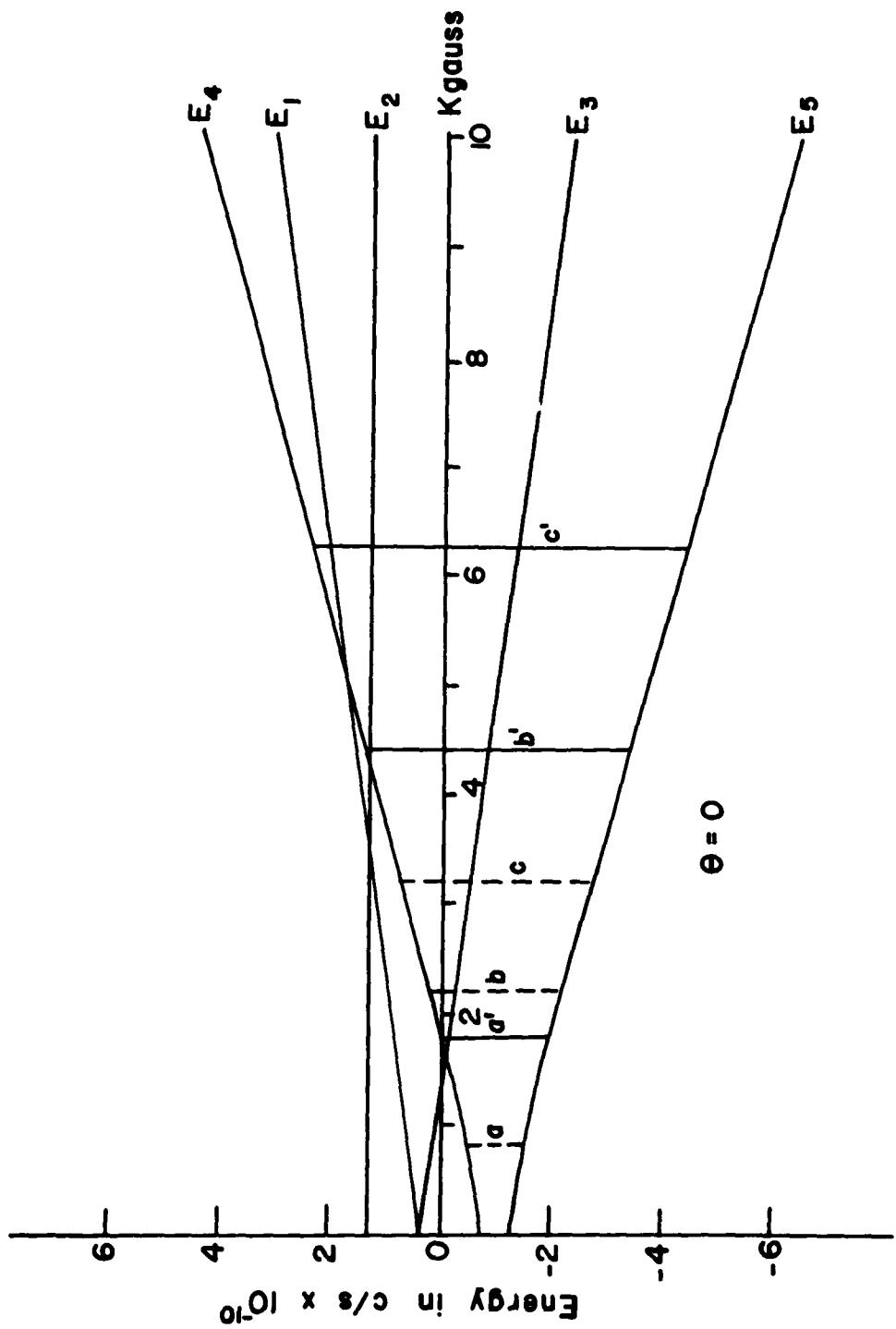


Figure III.3

be cocked relative to this four-fold axis of symmetry.

#### E. RESULTS.

The electron paramagnetic resonance experiments were carried out at 3 cm., 1 cm. and 8 mm. wavelengths and at the boiling point of liquid helium. The angular dependence at 1 cm. is shown in Figure III.4, which was obtained when the crystal was oriented so that a four-fold symmetry resulted. The observed lines could be fitted if it were assumed that the transitions correspond to

$$\text{Thus, } (hv)^2 = a^2 + 16 G^2 \cos^2 \Theta \quad (\text{III.3})$$

Using this expression  $a = 4446 \pm 9$  Mc/s. and  $g = 1.949$ .

The same lines were observed by Estle<sup>(6)</sup> who was able to obtain an independent of the orientation by doing the resonance at two different frequencies in the same cavity. His values are  $g = 1.937$  and  $a = 4506 \pm 6$  Mc/s.

Measurements were also made at 8 mm. which showed lines at approximately twice the expected field in addition to the expected lines. In addition during one run at one centimeter wavelength, the crystal was cocked at an angle which allowed the high field line to be observed. Unfortunately, the crystal could not be properly oriented and the results are only indicative that information may be obtained from more accurate measurements. However from the 1 cm. data the observed line may be fit if it is assumed that it arises from  $\Delta E = E_1 - E_3 = 2G \cos \Theta$ . Using this expression and Equation III.3 we find that,

$$a^2 = (hv)^2 \left( 1 - \frac{4 \frac{H_1^2}{H_2^2}}{} \right) \quad (\text{III.4})$$

is the low field line and  $H_2$  is the corresponding high field line. The calculated value of  $a$  is  $4532 \pm 400$  Mc/s. for six angles. The agreement is good but the large error reflects the small intensity and difficulty in making good field measurements. It is believed that the high field lines are the  $E_1 - E_3$  transitions. Further work needs to be done to substantiate these conclusions. In particular, intensity and frequency measurements at 35 KMc/s must be made.

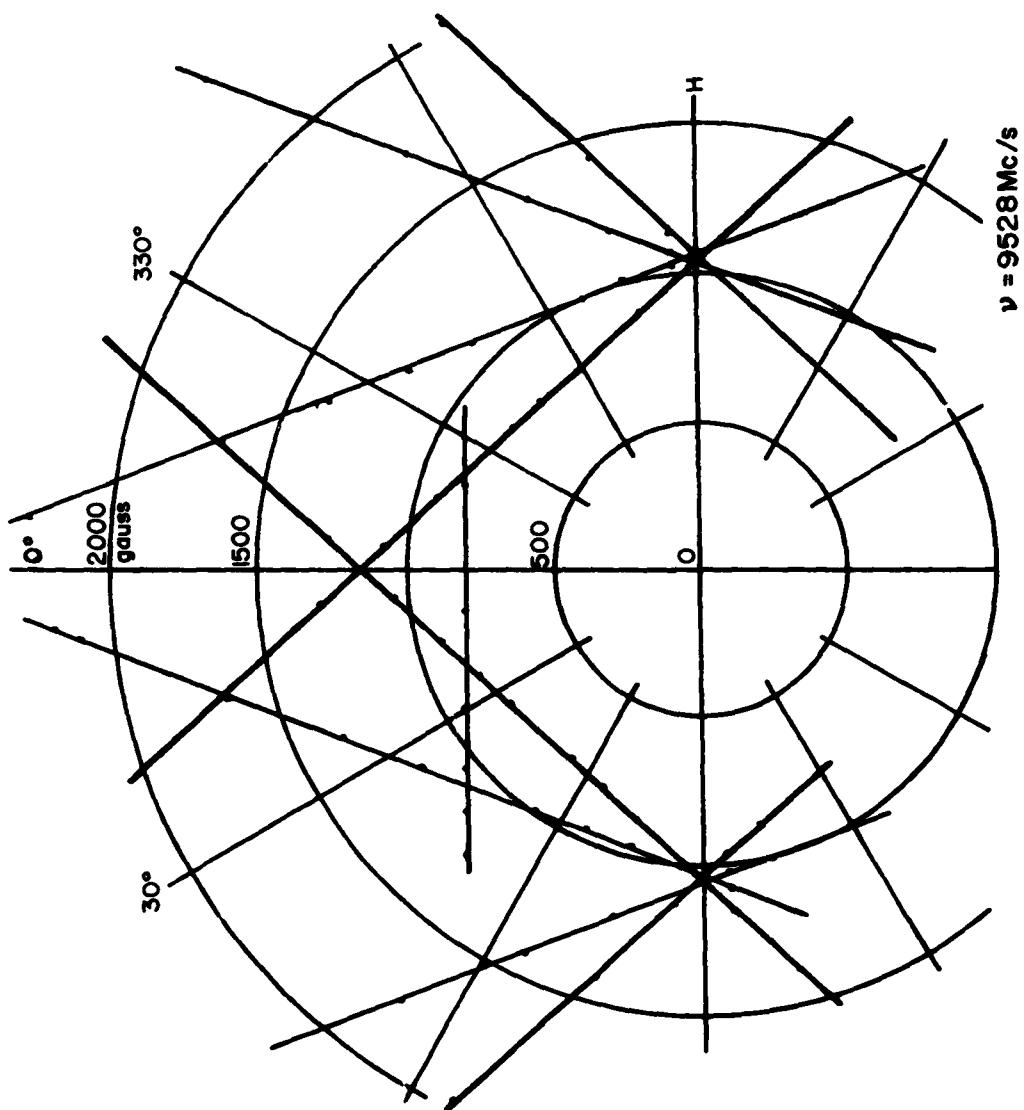


Figure III. 4

#### F. DISCUSSION OF RESULTS.

The measurements presented above are compatible with the picture of the ion in an octahedral interstitial site. In an octahedral field, the ground term of  $\text{Cr}^{+2}$  is  $t_{2g}^3 e_g \cdot 5E$  which breaks up into  $5A_1 + 5B_1$ . If we calculate within the  $5E$  state, an isotropic  $g$  value of 2.0023 is obtained. To the next approximation including mixing by spin-orbit interaction of the  $5T_{2g}$  term, it is found that

$$g_{11} = 2.0023 \text{ for } 5A_1$$

$$\text{and } g_{11} = 2.0023 - 2\lambda/\Delta \text{ for } 5B_1$$

where  $\Delta$  is the energy difference between the  $5E$  and  $5T_2$  levels. The one electron spin orbit coupling constant,  $\lambda$ , for  $d^4$  configurations equals  $230 \text{ cm}^{-1}$  for the free ion.

Pappalardo and Dietz at the Bell Telephone Laboratories reported an optical study on Cr in CdS. In general their spectral diagram indicates both interstitial and substitutional sites for the Cr ions. For a substitutional ion, they ascribe a peak at  $5,300 \text{ cm}^{-1}$  whereas there is also a peak at  $10,000 \text{ cm}^{-1}$ . We believe this peak at  $10,000 \text{ cm}^{-1}$  is the substitutional octahedral site because the value of  $\Delta$  for octahedral fields is approximately twice that for tetrahedral fields of the same ion. Also  $\Delta$  for  $\text{H}_2\text{O}$  is approximately  $13,900 \text{ cm}^{-1}$ . Since the ligand field of sulfide ions must be less, the value of  $10,000$  wave numbers is not unreasonable. Using this value the calculated values of  $g_{11}$  are 2.0023 for  $5A_1$  and 1.956 for  $5B_1$ . Therefore this model predicts the  $5B_1$  term in lowest which means that, since  $5B_1$  transforms like  $x^2 - y^2$ , the distortion is a squashing effect.

An estimate of the value of the  $D$  parameter may be also made. If the spin-orbit interaction of the ground state with the  $5T_2$  and  $t_{2g}^4 3T_1$  states are considered, the value of  $D$  is,

$$- 3/16 \frac{\lambda^2}{\Delta} - \frac{\lambda^2}{5E} \quad (\text{III.5})$$

where  $\lambda$  is the spin orbit coupling constant and  $E$  is the energy difference between the ground state and the  $^3T_1$  level. In terms of Racah coefficents,

$E = 6B + 5c - \Delta$  where  $\Delta$  is the cubic field splitting parameter. The value of  $E$  is  $12,100 \text{ cm}^{-1}$  and the calculated value of  $D$  is  $-2.08 \text{ cm}^{-1}$ .

The paramagnetic resonance lines at  $0.8 \text{ cm}$  wavelength support the calculated value of  $D$ , but more work needs to be carried out to accurately assign  $D$ .

The work of Estle is in disagreement with these conclusions. At low temperatures he finds a superhyperfine interaction of the d electrons with cadmium nuclei with the large interaction constant of six gauss. The pattern of lines obtained indicated that not less than six cadmium nuclei are involved. He therefore interprets the spectrum as resulting from a chromium (II) ion in a substitutional lattice site with a Jahn-Teller distortion along directions bisecting the lines to nearest neighbor sulfide ions.

The conflict between these two views needs to be resolved. It is planned to perform accurate measurements at  $8 \text{ mm}$  wavelengths and accurately measure the value of  $D$ . The value of  $D$  from Estle's model will be considerably lower because  $\Delta$  is larger.

#### IV. ANGULAR MODULATION OF MAGNETIC FIELDS IN PARAMAGNETIC RESONANCE EXPERIMENTS.

During the course of some experiments of the electron paramagnetic resonance of  $\text{Cr}^{+2}$  in  $\text{CdS}$  single crystals with a 100-Kc modulation system a number of inverted curves were observed as well as normal derivatives. The 100-kc modulation of the magnetic field was provided by a small loop in a rectangular cavity such that the direction of modulation was perpendicular to the  $H$  field. The dc magnetic field was rotated about an axis while the cavity assembly was fixed in the laboratory. Consequently, the modulation field was not necessarily parallel to the dc field and schematically is represented in Figure IV.1.

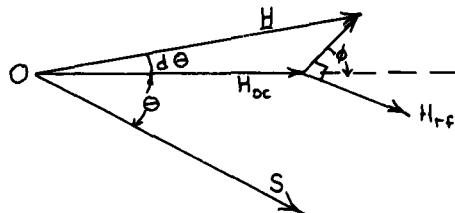


Figure IV.1. A vector diagram of the various fields in a typical experimental arrangement.  $H_{dc}$  is the external magnetic field,  $H_m$  is the modulation magnetic field,  $H_{rf}$  is the microwave magnetic field and  $S$  is the symmetry axis of the crystal exhibiting electron resonance.

Many Zeeman levels are angular dependent and we may represent the absorption of microwave power as a function of  $H$  and  $\theta$ , the angle between the magnetic field and the symmetry axis,

$$A = pA(H, \theta) \quad (\text{IV.1})$$

where  $p$  is the transition probability. The usual method of detection is to observe the derivative of absorption with magnetic field.

$$\Delta A = p \left\{ \left( \frac{\partial A}{\partial H} \right)_\theta \Delta H + \left( \frac{\partial A}{\partial \theta} \right)_H \Delta \theta \right\} \quad (\text{IV.2})$$

From Figure IV.1 we see that for  $H_m \ll H_{dc}$

$$\Delta \theta \sim \left( \frac{H_m}{H_{dc}} \right) \sin \phi \quad (\text{IV.3})$$

$$\Delta H \sim H_m \cos \phi$$

where  $H_m = H_m^* e^{i\omega t}$ . Substituting (IV.3) into (IV.2) we obtain

$$\Delta A = B_p [\cos \phi + (\sin \phi / H_{dc}) (\partial H / \partial \theta)_A] \quad (IV.4)$$

where  $B = H_m (\partial A / \partial H)_\theta$ . For  $\text{Cr}^{+2}$  in  $\text{CdS}$ , the ground state has an effective spin of 2. The transitions are observed between  $|a\rangle = |2\rangle + |2\rangle$  and  $|b\rangle = |2\rangle - |2\rangle$  and the transition probability is proportional to  $\cos^2 \alpha$ , where  $\alpha$  is the angle between  $H_{rf}$  and the symmetry axis. The magnetic field dependence of absorption is given by

$$\Delta A = B_p [\cos \phi + \sin \phi \tan \theta] \quad (IV.5)$$

where the right-hand side is a constant for a given microwave frequency  $\nu$  and zero field splitting  $\gamma_0$ . Substitution of (5) into (4) gives

$$\Delta A = B_p [\cos \phi + \sin \phi \tan \theta] \quad (IV.6)$$

It is easy to see that  $\Delta A$  can change sign depending upon  $\phi$  and  $\theta$ . It is also clear from (6) that angular modulation can separate angularly dependent resonance lines from angularly independent lines if  $\phi = \pi/2$ , i.e., the modulation loop is perpendicular to  $H_{dc}$ .

Two experiments were performed which generally agree with (IV.6). The cavity was modified so that the crystals could be rotated in the plane of  $H_{dc}$  a minimum for which  $\theta = 0$  and  $\phi$  ranged from 0 to  $\pi/2$ . From (6) we have

$$A = B_p \cos \phi$$

In this case since  $H_{dc}$  is along the symmetry axis, therefore  $\alpha = \pi/2 - \phi$  and  $p \sim \sin^2 \phi$  so that the intensity is proportional to  $\sin^2 \phi \cos \phi$ .

The results are plotted in Figure IV.2 which shows general agreement within the experimental error.

The second experiment was to fix  $\theta$  and measure the ratio of intensities when  $H_{rf}$  was parallel and perpendicular to  $H_{dc}$ . The calculated ratio is

$$\frac{P_{11}}{P_1} \tan \theta = \frac{\cos^2 \theta}{\sin^2 \theta} \tan \theta = 2 \text{ for } \theta = 24^\circ$$

The measured ratio was 2.1.

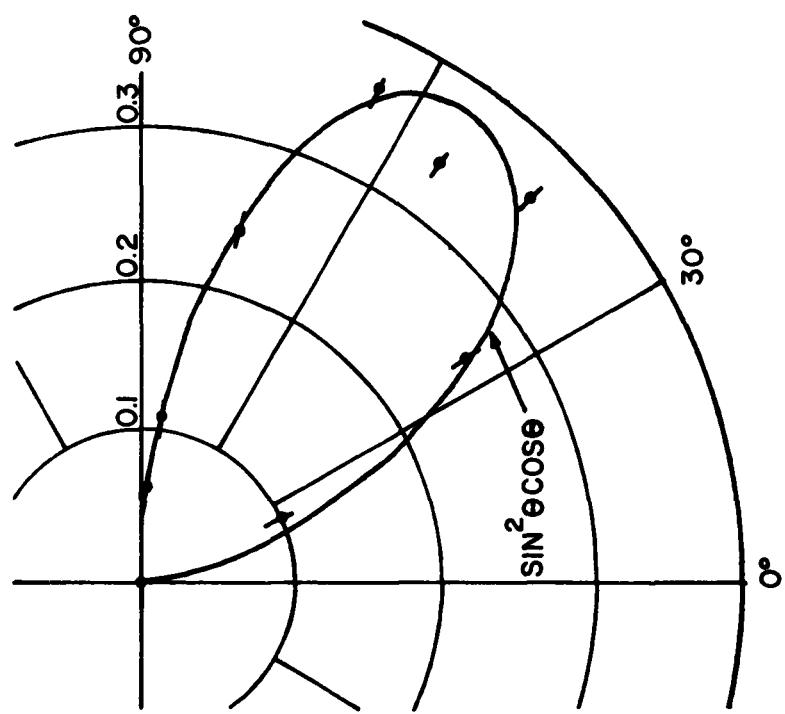


Figure IV. 2

## V. CADMIUM OXIDE PREPARATION.

### A. INTRODUCTION.

Recently, it has been desirable to find a host lattice for electron paramagnetic resonance measurements which would have a convenient type of nearest neighbor nucleus showing superior hyperfine interaction with impurity atom electrons. One of the possibilities was cadmium oxide which crystallizes in a face centered cubic lattice of the NaCl type. In addition 25% of the natural abundance of cadmium ore isotopes with a nuclear spin of  $1/2$  and approximately identical nuclear moments. Cadmium oxide is seemingly an ideal host lattice for these measurements and a program with Mr. Donald Locker of the Aeronautical Research Laboratory was carried out to grow these crystals.

### B. DESCRIPTION OF METHOD.

The method used was to weigh out approximately twenty grams of cadmium metal into a stainless steel tube which was then crimped at both ends. The tube was placed in an alumina furnace tube and heated to  $950^{\circ}\text{C}$  for a few hours. At this temperature, the vapor pressure of cadmium metal is several atmospheres and tends to release this pressure by leaking through the crimping. The small stream reacts with air and forms  $\text{CdO}$  single crystals near the crimped ends. Variations of temperature and atmosphere seems to have little effect on the crystal formation although  $950^{\circ}\text{C}$  seems to be an optimum temperature.

The necessity of stainless steel is not fully understood since the same treatment with zinc metal produces extensive corrosion of the tube. It is clear that materials such as quartz and "Vycor" are not suitable since  $\text{CdO}$  is a basic oxide which reacts to form a silicate.

### C. ANALYSIS.

A rotating crystal X-ray analysis was performed on the crystals formed from several runs. The measured lattice spacing agrees with the accepted

value of 4.69 Å to within the experimental error.

Samples of crystals were dissolved in HCl and polarographic analyses were made for cadmium. The polarograph was standardized against known quantities of CdCl<sub>2</sub> solutions. The results indicated that the cadmium content was stoichiometric within 0.5% for CdO.

#### D. OPTICAL MEASUREMENTS.

A thin platelet was found which was used for optical measurements of the absorption spectrum. A Cary Model 14 spectrograph was used. The crystal exhibited a window at 1.4 e.v. This value is to be compared with that measured on films of 2.3 e.v.

#### E. RESONANCE RESULTS.

Measurements of the conductivity of these crystals show them to be n-type and have a resistivity of 1 ohm - cm. Unfortunately this high conductivity reduces the Q of a microwave cavity with the result that electron paramagnetic resonance measurements can not be carried out successfully.

It appears that the high conductivity of the material is due to excess Cd metal which if removed will make the crystals suitable for resonance measurements.

## VI. COPPER (II) AND SILVER (II) IN ALKALI FLUORIDES.

### A. INTRODUCTION.

There has long been interest in the electron paramagnetic resonance of  $d^9$  configuration ions in alkali fluorides. The difficulty has been that upon heating copper (II) or silver (II) a reduction occurs to the +1 state which is diamagnetic.

It was felt however if a diffusion technique was used in a fluorine atmosphere and alkali fluorides were used as the crystalline host, that success might be obtained.

### B. COPPER (II).

Copper was successfully diffused into LiF by starting with copper metal between two plates of LiF. The temperature was kept at just below the melting point of LiF for several hours in a pressure of 2-3 atmosphere of  $F_2$ .

The resonance was observed at 3 cm. wavelength and at liquid nitrogen temperature. The spectrum can be interpreted as arising from a tetragonal distortion of the lattice around the copper ion.

The distortion occurs along the three principal cubic axes so that there are three possible  $Cu^{+2}$  sites. The resulting ground state doublet may be expressed by  $g^2 = g_{11}^2 \cos^2\theta + g_1^2 \sin^2\theta$ . It is found that  $g_1 = 2.079$ ,  $g_{11} = 2.467$ . No hyperfine interaction was observed.

### C. SILVER (II).

Diffusion of Ag(II) into NaF was accomplished in the same manner as described for copper. The electron paramagnetic resonance of silver (II) in NaF is much more complicated than that for copper. There appear to be several distortion axes among which are the principal axes and the three fold body diagonal axes. More work needs to be done on these materials before meaningful data results.

### D. HYPERFINE INTERACTION.

Neither Ag(II) nor Cu(II) prepared as outlined give hyperfine interaction spectra. In contrast, the spectra of  $Ag^{+2}$  prepared by irradiation of Ag(I) in

KCl show hyperfine interaction. The reason for this may possibly be due to a mechanism involved by Stevens which involves admixture of p orbitals to the d orbitals when there is a nearest neighbor lattice vacancy into which the d electrons may move. This has the effect of cancelling the electron density of the d electron at the silver nucleus and reducing the hyperfine interaction. Double resonance experiments should be able to distinguish whether or not the effect is real.

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